This section describes the results, data analysis, probable constituent sources, and recommendations for the 2008-2009 Monitoring Program.

4.1 HYDROLOGY: PRECIPITATION AND FLOW

This section discusses the precipitation and flow data and the hydrologic analysis of the monitoring area. Precipitation data and hydrographs can be used to address the following management question:

How did the 2008-2009 storm season differ in comparison to previous storm seasons?

This is addressed in two ways:

1. Figure 4-1 is a comparison of the total monthly rainfall for the 2008-2009 storm season and the long-term pattern of rainfall observed in downtown Los Angeles at Station 716, Ducommun Street. The 2008-2009 storm season was wetter than average in the early months (November and December), but drier throughout the remaining season. In 2009, January and March were uncharacteristically dry (less than 15 percent of the storm seasons have experienced drier Januarys or Marches than in 2009). January 2009 only received 0.40 inches in comparison to the 3.34 inch - 138 year average, representing only 11.97 percent of this average. March 2009 received 0.24 inches, only 8.80 percent of average rainfall (2.73 inches) for this month.

2. Figure 4-2 illustrates that the total annual rainfall of 8.08 inches during the 2008-2009 storm season in downtown Los Angeles was 52.12 percent of the 138 year average annual rainfall, 15.50 inches.

Hydrographs are provided for all monitoring station events for which flow-weighted composite samples were collected during the 2008-2009 monitoring year (Appendix A). Each hydrograph includes the known times of the first and last composite sample aliquot collection, the sample volume interval, runoff volume, and the percent of storm sampled.

For several hydrographs, including those for D.D.I 8 (TS23) during 2008-09Event03 and Ballona Creek (S01) during 2008-09Event26, the data showed a much shorter sampling interval than was actually collected. In these instances, the percentage of the storm sampled appeared to be less than one percent, which was not the case; the actual last composite sample should have plotted far to the right of the plotted location, indicating a much larger percent of the storm captured. The reason for this is unknown but believed to be a data transfer error. Other than these instances, the hydrographs and composite sampling start and end times can be used to address the following management questions:

What percentage and what portion of the storm event was sampled?

This question is answered by examining the hydrographs (Appendix A). Each hydrograph contains the percent of the storm that was sampled and the first and last composite samples, which provides a visual representation of the sampled portion of the storm, in most cases.

To the extent possible, the initial portion of the event was sampled, rather than the tailing end of the hydrographs. Typically the percent sampled was in the range of 40 to 80 percent. Sampling the initial portion of the storm could bias load estimates higher than the true value, if constituent concentrations are higher during the initial portion of the storm.

4.2 STORM WATER QUALITY

4.2.1 Comparison to Water Quality Objectives

The Los Angeles Flood Control District (LACFCD) met the requirement to compare results to applicable water quality standards by evaluating and compiling a list of applicable numeric water quality objectives, and comparing results measured to the applicable objectives.

The key management question that this section addresses is:

What constituents are measured at concentrations that do not attain water quality objectives?

The monitoring requirements of the permit require that exceedances of water quality standards[1] be highlighted. Water quality standards consist of defined beneficial uses of water, and numeric or narrative water quality objectives used to evaluate whether beneficial uses are protected. Numeric water quality objectives are expressed in terms of:

- Magnitude – the threshold concentration at which beneficial uses are threatened or impaired);
- Frequency – the number of exceedances of threshold concentrations in a given time period that indicates impairment; and
- Duration – the length of time the ecosystem is exposed to concentrations above the threshold.

All analyses that compare measurements to objectives consider the magnitude. Aquatic life objectives established in the California Toxics Rule (CTR) also allow an exceedance frequency of no more than once every three years (USEPA, 2000; see page 31,700 of

[1] Exceedance of water quality standards is assumed when numeric water quality objectives are not attained

Federal Register Volume 65 Number 97) Human health – based objectives, such as mercury in the CTR or Maximum Contaminant Levels (MCLs) cited in the Los Angeles Regional Water Quality Control Plan (the Basin Plan), do not specify an exceedance frequency.

The duration for many aquatic life objectives (e.g., WARM, COLD) is usually expressed as acute (1-hour exposure) or chronic (4-day exposure). Some objectives (e.g., ammonia) are expressed as 30-day averages, or other averaging periods. Some objectives (e.g., human – health criteria in the CTR) are expressed as instantaneous thresholds. For this assessment, all analyses performed were on based on 24 hour composite samples or instantaneous grab samples. Therefore, only comparisons to acute water quality objectives are made.

Two categories of water quality objectives were identified: Category 1 and Category 2. Category 1 water quality objectives (see table below) are those for which there is no uncertainty about the applicable objectives, or the implementation with respect to frequency and duration. Category 2 water quality objectives are those for which there is uncertainty about the applicability of the beneficial use (e.g., the conditional use of municipal water supply), or uncertainty about implementation of the objective (e.g., 4-day averaging periods).

The numeric objectives in the table below that are listed as ranges are calculated values based on site specific conditions. Ammonia concentrations are calculated using measured pH and Tables 3-1 (COLD) and 3-2 (WARM) of the Basin Plan, assuming a temperature of 25 °C (for COLD) and 20 °C (for WARM). Dissolved metals concentrations are calculated using measure hardness and procedures set forth in the CTR. The ranges shown reflect calculated objectives for the period of 2006 through 2009 at all mass emission and tributary stations.

Category 1 Numeric Objectives Used to Evaluate Attainment of Water Quality Standards

Constituent	Numeric Objective	Unit	Reference	Beneficial Use
Chloride	Ballona Creek (S01) None Malibu Creek (S02) < 500 Los Angeles River (S10) < 150 Coyote Creek (S13) None San Gabriel River (S14)< 150 Dominguez Channel (S28) None Santa Clara River (S29) < 150	mg/L	Basin Plan	Groundwater recharge (GWR), general water quality indicators
Sulfate	Ballona Creek (S01) None Malibu Creek (S02) < 500 Los Angeles River (S10) < 350 Coyote Creek (S13) None San Gabriel River (S14) < 300 Dominguez Channel (S28)None Santa Clara River (S29) < 600	mg/L	Basin Plan	
TDS	Ballona Creek (S01) None Malibu Creek (S02) < 2,000 Los Angeles River (S10) < 1,500 Coyote Creek (S13) None San Gabriel River (S14) <750 Dominguez Channel (S28) None Santa Clara River (S29) < 1,200	mg/L	Basin Plan	
pH	6.5 - 8.5	None	Basin Plan	Aquatic life habitat (WARM, COLD)
DO	(All) > 5 (WARM) (Malibu Creek) > 6 (COLD) (Malibu Creek) > 7 (SPAWN)	mg/L	Basin Plan	Aquatic life habitat
Fecal Coliform	< 400	mpn/ 100 ml	Basin Plan	Water contact recreation (REC-1) (wet weather suspension in Ballona Creek, Los Angeles River, Coyote Creek, San Gabriel River, Dominguez Channel)[1]

[1] Wet weather suspension applies to 2008-09Event06, 2008-09Event09, and 2008-09Event21.

Category 1 Numeric Objectives Used to Evaluate Attainment of Water Quality Standards (Continued)

Constituent	Numeric Objective	Unit	Reference	Beneficial Use
Ammonia	0.7 - 5 (COLD) 0.9 - 30 (WARM)	mg/L	Basin Plan	Aquatic life habitat (acute exposure only)
Cyanide	0.022	mg/L	CTR	
Dissolved Arsenic	340	µg/L	CTR	
Dissolved Cadmium	1-24	µg/L	CTR	
Dissolved Chromium +6	16	µg/L	CTR	
Dissolved Chromium	180 - 2,050	µg/L	CTR	
Dissolved Copper	4-61	µg/L	CTR	
Dissolved Lead	14 - 350	µg/L	CTR	
Dissolved Nickel	150 - 1,800	µg/L	CTR	
Dissolved Silver	0.3 - 60	µg/L	CTR	
Dissolved Zinc	40 - 450	µg/L	CTR	
Total Mercury	0.051	µg/L	CTR	Human health (fish consumption only)

Some constituents have water quality objectives based on municipal water supply (MUN), which is a conditional beneficial use in all monitored watersheds. For this reason, the water quality objectives applicable to MUN are included in Category 2 and are not used to compare monitoring results to water quality objectives.

Some constituents have chronic water quality objectives which are based on 4-day average exposures. Each measurement of this program is either based on a grab or a 24-hour composite sample. Therefore, chronic objectives are also included in Category 2 and are not used for comparison of monitoring data to water quality objectives.

Figures 4-3.1 through 4-3.17 show a complete summary of water quality trends for 2006-2007 through 2008-2009 monitoring for mass emission stations and for 2008-2009 monitoring for tributary stations for all constituents with Category 1 objectives, except dissolved silver. Plots of dissolved silver are not shown because all dissolved silver measurements were reported as -99, either because they were below the detection limit (77 samples) or below the reporting limit (15 samples). Details are discussed below.

4.2.1.1 Mass Emission Stations

This sub-section summarizes information about Category 1 water quality objectives not attained at Mass Emission Stations sampled during the 2008–2009 annual monitoring program. Results are grouped by wet weather and dry weather and by watershed. Specific results are available in Appendix B for all stations and sampling events.

The most common observances of water quality objectives that were not attained during wet weather events in highly urbanized watersheds were for dissolved copper and zinc. Fecal coliform was measured in excess of the numeric standard in wet weather in urban watersheds. The wet weather suspension applies in urban watersheds during storm events greater than 0.5 inches over 24 hours. In the 2008-2009 storm season, this applied to:

- 2008-09Event06 (November 25, 2008)
- 2008-09Event09 (December 15, 2008)
- 2008-09Event21 (February 5, 2009)

Measurements above the water quality objective were not highlighted for those three events. At times, fecal coliform water quality objectives were not attained during wet weather in some of the less developed watersheds and during dry weather in highly urbanized watersheds as well as in some less developed watersheds. Sulfate did not attain the water quality objective in Malibu Creek watershed. Cyanide did not attain the water quality objective in the Los Angeles River during dry weather. Mercury concentrations were reported in various watersheds at levels above the water quality objective. However, for reasons explained in the correlation analysis (Section 4.2.2), the mercury concentrations reported are believed to be biased high due to the analytical method used.

The following discussion of the Mass Emission Station results provides context for the instances where water quality objectives are not attained, where appropriate, including details such as the wet weather suspension of bacteria standards for water contact (LARWQCB, 2003), frequency over the past three years that measurements were above objectives, and whether the measurement above the objective was driven by variability in the constituent or the calculated objective.

When water quality objectives are not attained, any qualifiers provided by the analytical laboratory are identified. Laboratory analytical qualifiers noted on review of the data are:

- BMDL Below Method Detection Limit;
- BRL Below Reporting Limit;
- DNQ Detected not quantified.

BRL and DNQ are equivalent, and indicate that the reported values are estimates because they are close to the detection limit. BMDL signifies that the detected concentration is below the analytical instruments threshold for differentiating a true measurement from background noise. In this analysis, reported values higher than the water quality objective are not discounted based on the three qualifiers above. Rather, the qualifiers are provided so that decision makers can understand the reliability of data used to assess any impairment, and identify whether improved analytical methods are warranted.

Wet Weather

Ballona Creek (S01)

A summary of constituents not attaining Category 1 water quality objectives at the Ballona Creek Mass Emission Station (Ballona Creek) during the 2008–2009 wet weather sampling is presented in Table 4-4.1 and follows. All plots shown (Figure 4-3.1 through 4-3.17) cover three years of monitoring data (2006-2009), although the only instances of non-attainment discussed are from 2008–2009.

Fecal coliform bacteria did not attain the applicable water quality objective (400 mpn/100 ml) five out of five times sampled during wet weather in Ballona Creek (Figure 4-3.7). Ballona Creek is subject to the wet weather suspension of the REC-1 beneficial use (water contact recreation – full immersion) during high flow periods, and therefore measurements above the water quality objective are not highlighted for events 2008-09Event06, 2008-09Event09, and 2008-09Event21.

Dissolved copper did not attain the hardness-based water quality objective (7.5 to 36 µg/L) during wet weather at Ballona Creek for three of the five events measured (Figure 4-3.8). Inspection of dissolved copper and hardness values Table 4-4.1 shows that dissolved copper concentrations were fairly consistent (median of 10 µg/L, range of 9 to 13 µg/L). In contrast, the hardness at Ballona Creek is much more variable (median of 70 mg/L, range of 50 to 280 mg/L). Thus, relatively constant dissolved copper concentrations did not attain site-specific objectives during critical conditions of low hardness during wet weather in Ballona Creek. Two of the dissolved copper measurements above the water quality objective were based on values that were qualified as Below Method Detection Limit (BMDL).

Dissolved zinc did not attain the hardness-based water quality objective (65 to 460 µg/L) during wet weather at Ballona Creek for one of the five events measured (Figure 4-3.17). Dissolved zinc concentrations are also relatively constant (median of 55 µg/L, range of 38 to 67 µg/L). The instance when zinc did not attain the objective occurred during a critical condition of low hardness, when the calculated objective was at a minimum.

Total mercury did not attain the human health water quality objective (0.051 µg/L) on one of the five events measured in Ballona Creek during wet weather (Figure 4-3.12). The analysis was qualified as “detected but not quantified” (DNQ) by the laboratory. As explained below (See Section 4.2.2, correlation analysis) the reported measurement of mercury above the water quality objective is believed to be due to bias added by the analytical method used.

Malibu Creek (S02)

A summary of constituents not attaining Category 1 water quality objectives at the Malibu Creek Mass Emission Station (Malibu Creek) during the 2008–2009 wet weather sampling is presented in Table 4-4.2 and follows. All plots shown (Figure 4-3.1 through 4-3.17) cover three years of monitoring data (2006-2009), although the only measurements above the water quality objective discussed are from 2008–2009.

Unlike years past, fecal coliform bacteria did not attain the applicable water quality objective (400 mpn/100 ml) three out of four times measured during wet weather in Malibu Creek (Figure 4-3.7). Malibu Creek is not subject to the wet weather suspension of the REC-1 beneficial use.

Sulfate did not attain the watershed-specific water quality objective (500 mg/L) in two out of five wet weather events sampled in Malibu Creek. Total dissolved solids (TDS) did not attain the watershed-specific water quality objective (2000 mg/L) once out of five wet weather events sampled.

Total mercury did not attain the human health water quality objective (0.051 µg/L) on one of the five events measured in Malibu Creek during wet weather (Figure 4-3.12). The analysis was qualified DNQ by the laboratory. As explained below (See Section 4.2.2, correlation analysis) the reported measurement of mercury above the water quality objective is believed to be due to bias added by the analytical method used.

Los Angeles River (S10)

A summary of constituents not attaining Category 1 water quality objectives at the Los Angeles River Mass Emission Station (Los Angeles River) during the 2008–2009 wet weather sampling is presented in Table 4-4.3 and follows. All plots shown (Figure 4-3.1 through 4-3.17) cover three years of monitoring data (2006-2009), although the only measurements above the water quality objective discussed are from 2008–2009.

Fecal coliform bacteria did not attain the applicable water quality objective (400 mpn/100 ml) five out of five times sampled during wet weather in Los Angeles River (Figure 4-3.7). Los Angeles River is subject to the wet weather suspension of the REC-1 beneficial use, and therefore measurements above the water quality objective are not highlighted for events 2008-09Event06, 2008-09Event09, and 2008-09Event21.

Dissolved copper concentrations did not attain the hardness-based water quality objective (3.6 to 61.2 µg/L) once out of the four wet weather events measured (Figure 4-3.8). Dissolved copper concentrations are somewhat variable (median 10 µg/L, ranging from 6 to 15 µg/L). The event measurement of 9.7 µg/L, close to the median concentration, did not attain the lowest hardness-base objective (3.6 µg/L) of all wet weather events measured in 2008–2009. The measurement was qualified as BMDL.

Dissolved zinc concentrations did not attain the hardness-based water quality objective (36 to 460 µg/L) once out of the four wet weather events measured (Figure 4-3.17). Dissolved zinc concentrations are somewhat variable (median 48 µg/L, ranging from 30 to 78 µg/L). The event measurement of 57.5 µg/L, close to the median concentration, did not attain the lowest hardness-base objective (36 µg/L) of all wet weather events measured in 2008–2009. The measurement above the water quality objective occurred in the same event (2008-09Event23, February 13, 2009) as the dissolved copper measurement above the water quality objective in the Los Angeles River. The measurement was qualified as BMDL.

The CTR allows an exceedance frequency of no more than once every three years for aquatic life criteria. Both copper (Figure 4-3.8) and zinc (Figure 4-3.17) have previously not attained the acute water quality objective within the past three years.

Coyote Creek (S13)

A summary of constituents not attaining Category 1 water quality objectives at the Coyote Creek Mass Emission Station (Coyote Creek) during the 2008–2009 wet weather sampling is presented in Table 4-4.4. All plots shown (Figure 4-3.1 through 4-3.17) cover three years of monitoring data (2006-2009), although the only measurements above the water quality objective discussed are from 2008–2009.

Fecal coliform bacteria did not attain the applicable water quality objective (400 mpn/100 ml) five out of five times sampled during wet weather in Coyote Creek (Figure 4-3.7). Coyote Creek is subject to the wet weather suspension of the REC-1 beneficial use, and therefore measurements above the water quality objective are not highlighted for events 2008-09Event06, 2008-09Event09, and 2008-09Event21.

All other Category 1 water quality objectives were attained during 2008–2009 wet weather events sampled.

San Gabriel River (S14)

A summary of constituents not attaining Category 1 water quality objectives at the San Gabriel River Mass Emission Station (San Gabriel River) during the 2008–2009 wet weather sampling is presented in Table 4-4.5. All plots shown (Figure 4-3.1 – 4-3.17) cover three years of monitoring data (2006-2009), although the only measurements above the water quality objective discussed are from 2008–2009.

Fecal coliform bacteria did not attain the applicable water quality objective (400 mpn/100 ml) four out of five times sampled during wet weather in San Gabriel River (Figure 4-3.7). San Gabriel River is subject to the wet weather suspension of the REC-1 beneficial use, and therefore measurements above the water quality objective are not highlighted for events 2008-09Event06, 2008-09Event09, and 2008-09Event21.

Total mercury did not attain the human health water quality objective (0.051 µg/L) on one of the five events measured in San Gabriel River during wet weather (Figure 4-3.12). The analysis was qualified as DNQ by the laboratory. As explained below (See Section 4.2.2, correlation analysis) the reported measurement of mercury above the water quality objective is believed to be due to bias added by the analytical method used.

Dominguez Channel (S28)

A summary of constituents not attaining Category 1 water quality objectives at the Dominguez Channel Mass Emission Station (Dominguez Channel) during the 2008–2009 wet weather sampling is presented in Table 4-4.6. All plots shown (Figure 4-3.1 through 4-3.17) cover three years of monitoring data (2006-2009), although the only measurements above the water quality objective discussed are from 2008–2009.

Fecal coliform bacteria did not attain the applicable water quality objective (400 mpn/ 100 ml) five out of five times sampled during wet weather in Dominguez Channel (Figure 4-3.7). Dominguez Channel is subject to the wet weather suspension of the REC-1 beneficial use, and therefore measurements above the water quality objective are not highlighted for events 2008-09Event06, 2008-09Event09, and 2008-09Event21.

Dissolved copper concentrations did not attain the water quality objective in all five wet weather events measured in Dominguez Channel (Figure 4-3.8). Dissolved copper concentrations in Dominguez Channel are somewhat higher compared to other mass emission stations (median 14 µg/L, ranging from of 14 to 22 µg/L). Two of the wet weather measurements were qualified as BRL; the other three were qualified as BMDL.

Dissolved zinc concentrations did not attain the water quality objective in all five wet weather events measured in Dominguez Channel (Figure 4-3.17). Dissolved zinc concentrations in Dominguez Channel are generally higher compared to other mass emission stations (median 88 µg/L, ranging from of 83 to 148 µg/L). Two of the wet weather measurements were qualified as BRL; the other three were qualified as BMDL.

Total mercury did not attain the human health water quality objective (0.051 µg/L) on one of the five events measured in Dominguez Channel during wet weather (Figure 4-3.12). The analysis was qualified as DNQ by the laboratory. As explained below (See Section 4.2.2 Correlation Analysis), the reported mercury measurements are believed to be biased high due to bias added by the analytical method used.

Santa Clara River (S29)

A summary of constituents not attaining Category 1 water quality objectives at the Santa Clara River Mass Emission Station (Santa Clara River) during the 2008–2009 wet weather sampling is presented in Table 4-4.7. All plots shown (Figure 4-3.1 through 4-3.17) cover three years of monitoring data (2006-2009), although the only measurements above the water quality objective discussed are from 2008–2009.

Fecal coliform bacteria did not attain the applicable water quality objective (400 mpn/100 ml) four out of five times sampled during wet weather in Santa Clara River (Figure 4-3.7). Santa Clara River is not subject to the wet weather suspension of the REC-1 beneficial use.

Dry Weather

Ballona Creek (S01)

A summary of constituents not attaining Category 1 water quality objectives at Ballona Creek during the 2008–2009 dry weather sampling is presented in Table 4-4.1. All plots shown (Figure 4-3.1 – 4-3.17) cover three years of monitoring data (2006-2009), although the only measurements above the water quality objectives discussed are from 2008–2009.

Fecal coliform bacteria did not attain the applicable water quality objective (400 mpn/ 100 ml) two out of three times sampled during dry weather in Ballona Creek (Figure 4-3.7).

Total mercury did not attain the human health water quality objective (0.051 µg/L) two out of the three times measured in Ballona Creek during dry weather (Figure 4-3.12). The analysis was qualified as “detected but not quantified” (DNQ) by the laboratory. As explained below (See Section 4.2.2, correlation analysis) the reported measurement of mercury above the water quality objective is believed to be due to bias added by the analytical method used.

Malibu Creek (S02)

A summary of constituents not attaining Category 1 water quality objectives at Malibu Creek during the 2008–2009 dry weather sampling is presented in Table 4-4.2. All plots shown (Figure 4-3.1 through 4-3.17) cover three years of monitoring data (2006-2009), although the only measurements above the water quality objectives discussed are from 2008–2009.

Sulfate did not attain the watershed-specific water quality objective (500 mg/L) in two out of three dry weather events sampled in Malibu Creek.

Total mercury did not attain the human health water quality objective (0.051 µg/L) on one of the three events measured in Malibu Creek during dry weather (Figure 4-3.12). The analysis was qualified DNQ by the laboratory. As explained below (See Section 4.2.2, correlation analysis) the reported measurement of mercury above the water quality objective is believed to be due to bias added by the analytical method used.

Los Angeles River (S10)

A summary of constituents not attaining Category 1 water quality objectives at Los Angeles River during the 2008–2009 dry weather sampling is presented in Table 4-4.3. All plots shown (Figure 4-3.1 – 4-3.17) cover three years of monitoring data (2006-2009), although the only measurements above the water quality objectives discussed are from 2008–2009.

Cyanide did not attain the CTR acute water quality objective (0.022 µg/L) in one of the three dry weather events measured (Figure 4-3). The CTR allows an exceedance frequency of no more than once every three years for aquatic life criteria. Cyanide has previously not attained the acute water quality objective within the past three years in the Los Angeles River.

The Basin Plan pH upper limit of 8.5 was not attained twice out of the three dry weather events monitored (Figure 4-3.14). Fecal coliform bacteria did not attain the applicable water quality objective (400 mpn/100 ml) one out of three times sampled during dry weather in Los Angeles River (Figure 4-3.7).

Coyote Creek (S13)

A summary of constituents not attaining Category 1 water quality objectives at Coyote Creek during the 2008–2009 dry weather sampling is presented in Table 4-4.4. All plots shown (Figure 4-3.1 through 4-3.17) cover three years of monitoring data (2006-2009), although the only measurements above the water quality objectives discussed are from 2008–2009.

The Basin Plan pH upper limit of 8.5 was did not attain once out of the three dry weather events monitored (Figure 4-3.14). Fecal coliform bacteria did not attain the applicable water quality objective (400 mpn/100 ml) one out of three times sampled during dry weather in Coyote Creek (Figure 4-3.7). All plots shown (Figure 4-3.1 through 4-3.17) cover three years of monitoring data (2006-2009), although the only measurements above the water quality objectives discussed are from 2008–2009.

San Gabriel River (S14)

A summary of constituents not attaining Category 1 water quality objectives at San Gabriel River during the 2008–2009 dry weather sampling is presented in Table 4-4.5. All plots shown (Figure 4-3.1 – 4-3.17) cover three years of monitoring data (2006-2009), although the only measurements above the water quality objectives discussed are from 2008–2009. All measurements are reported in Appendix B.

The Basin Plan pH upper limit of 8.5 was not attained once out of the three dry weather events monitored (Figure 4-3.14). Fecal coliform bacteria did not attain the applicable water quality objective (400 mpn/100 ml) two out of three times sampled during dry weather in Los Angeles River (Figure 4-3.7). Chloride and TDS each did not attain the watershed-specific Basin Plan water quality objective (150 mg/L) once out of the three times measured during dry weather. All plots shown (Figure 4-3.1 through 4-3.17) cover three years of monitoring data (2006-2009), although the only measurements above the water quality objectives discussed are from 2008–2009.

Dominguez Channel (S28)

A summary of constituents not attaining Category 1 water quality objectives at Dominguez Channel during the 2008–2009 dry weather sampling is presented in Table 4-4.6. All plots shown (Figure 4-3.1 – 4-3.17) cover three years of monitoring data (2006-2009), although the only measurements above the water quality objectives discussed are from 2008–2009.

The Basin Plan pH upper limit of 8.5 was not attained twice out of the three dry weather events monitored (Figure 4-3.14). Fecal coliform bacteria did not attain the applicable water quality objective (400 mpn/100 ml) one out of three times sampled during dry weather in Dominguez Channel (Figure 4-3.7).

Total mercury did not attain the human health water quality objective (0.051 µg/L) on one of the three events measured in San Gabriel River during dry weather (Figure 4-

3.12). As explained below (See Section 4.2.2, correlation analysis) the reported measurement of mercury above the water quality objective is believed to be due to bias added by the analytical method used.

Santa Clara River (S29)

A summary of constituents not attaining Category 1 water quality objectives at Santa Clara River during the 2008–2009 dry weather sampling is presented in Table 4-4.7. All plots shown (Figure 4-3.1 – 4-3.17) cover three years of monitoring data (2006-2009), although the only measurements above the water quality objectives discussed are from 2008–2009.

Fecal coliform bacteria measurements were above the applicable water quality objective (400 mpn/100 ml) one out of three times sampled during dry weather in Santa Clara River (Figure 4-3.7).

4.2.1.2 Tributary Stations

This sub-section summarizes information comparing constituent measurements to Category 1 water quality objectives at Tributary Stations sampled during the 2008–2009 year of the annual monitoring program. Results are grouped by wet weather and dry weather, and by watershed. Specific results are available in Appendix B for all stations and sampling events. The Tributary Stations were all located in the Dominguez Channel Watershed.

The most common wet weather measurements above the water quality objective were dissolved copper and zinc in this highly urbanized, industrial subwatershed. Fecal coliform objectives were not always attained at every tributary, during dry weather. The tributaries are assumed to be subject to the wet weather suspension of REC-1 and REC-2 beneficial uses applicable to Dominguez Channel. Although fecal coliform was measured in excess of the numeric objective in some events, these measurements were not highlighted in tables as non-attainments of water quality objectives when the storm event was greater than 0.5 inches of precipitation (2008-09Event06, 2008-09Event09, and 2008-09Event21). The pH objectives were not attained in wet weather and dry weather. Most, but not all of the wet weather pH measurements not attaining the water quality objective were the result of measurements below the minimum threshold of 6.5. All of the dry weather pH measurements not attaining the water quality objective were the result of pH values above the maximum threshold of 8.5. Mercury measurements above the water quality objective occasionally were reported. However, for reasons explained in the correlation analysis (Section 4.2.2) the reported measurement of mercury above the water quality objective is believed to be due to bias added by the analytical method used.

The following discussion of the Tributary Station results provide context, where appropriate, on details such as wet weather suspension of bacteria standards for water contact, comparison of results to the Dominguez Channel mass emissions station, and qualifiers noted by the analytical laboratory.

Wet Weather

Project No. 1232 (TS19)

A summary of constituents not attaining Category 1 water quality objectives at the Project No. 1232 Tributary Station (Project No. 1232) during the 2008–2009 wet weather sampling is presented in Table 4-5.1.

Fecal coliform bacteria measurements were above the applicable water quality objective (400 mpn/100 ml) five out of five times sampled during wet weather in (Figure 4-3.7). However, the Dominguez Channel tributaries are subject to the high flow suspension of REC-1 and REC-2 beneficial uses and standards in accordance with the “tributary rule” of the Basin Plan, as applicable to the Dominguez Channel, for events 2008-09Event06, 2008-09Event09, and 2008-09Event21. Those events are not highlighted as non-attainment of water quality objectives in data tables.

The pH measured at Project No. 1232 was below the Basin Plan limit of 6.5 once out of five times measured during wet weather sampling (Figure 4-3.14).

Dissolved copper concentrations at Project No. 1232 were above the water quality objective (4 to 61 µg/L) all five times it was measured during wet weather (Figure 4-3.8). Dissolved copper concentrations (median 14 µg/L, ranging from 10 to 29 µg/L) were comparable to those found Dominguez Channel. Three of those copper measurements were qualified as BMDL.

Dissolved zinc concentrations also were above the water quality objective (76 to 458 µg/L) in all five of the five wet weather events sampled (Figure 4-3.17). Zinc concentrations were comparable to Dominguez Channel (median of 130 µg/L, range of 112 to 158 µg/L). One of those zinc measurements was qualified as BRL while four were qualified as BMDL.

Total mercury measurements were reported above the human health water quality objective (0.051 µg/L) in one of the five events measured at Project No. 1232 during wet weather (Figure 4-3.12). As explained below (See Section 4.2.2, correlation analysis) the reported measurement of mercury above the water quality objective is believed to be due to bias added by the analytical method used.

PD 669 (TS20)

A summary of constituents not attaining Category 1 water quality objectives at the PD 669 Tributary Station (PD 669) during the 2008–2009 wet weather sampling is presented in Table 4-5.2. The pH at PD 669 did not attain the upper limit of 8.5 established in the Basin Plan once out of the five times measured in wet weather events (Figure 4-3.14).

Fecal coliform bacteria measurements were above the applicable water quality objective (400 mpn/100 ml) five out of five times sampled during wet weather in (Figure 4-3.7). However, the Dominguez Channel tributaries are subject to the high flow suspension of REC-1 and REC-2 beneficial uses and standards in accordance with the “tributary rule” of the Basin Plan, as applicable to the Dominguez Channel, for events 2008-09Event06, 2008-09Event09, and 2008-09Event21. Those events are not highlighted as non-attainment of water quality objectives in data tables. Dissolved copper measurements were above the hardness-based water quality objective (10 to 61 µg/L) twice out of the five times measured (Figure 4-3.8). Dissolved copper concentrations (median 11 µg/L, ranging from 8 to 18 µg/L) were comparable to Dominguez Channel. One of those measurements was qualified as BMDL.

Project Nos. 5246 & 74 (TS21)

A summary of constituents not attaining Category 1 water quality objectives at the Project Nos. 5246 & 74 Tributary Station (Project Nos. 5246 & 74) during the 2008–2009 wet weather sampling is presented in Table 4-5.3.

The pH at Project Nos. 5246 & 74 did not attain the upper limit of 8.5 established in the Basin Plan once out of the five times measured in wet weather events (Figure 4-3.14).

Fecal coliform bacteria measurements were above the applicable water quality objective (400 mpn/100 ml) five out of five times sampled during wet weather in (Figure 4-3.7). However, the Dominguez Channel tributaries are subject to the high flow suspension of REC-1 and REC-2 beneficial uses and standards in accordance with the “tributary rule” of the Basin Plan, as applicable to the Dominguez Channel, for events 2008-09Event06, 2008-09Event09, and 2008-09Event21. Those events are not highlighted as non-attainment of water quality objectives in data tables.

Dissolved copper concentrations did not attain the water quality objective (6 to 61 µg/L) all five times it was measured during wet weather (Figure 4-3.8). Dissolved copper concentrations (median 17 µg/L, ranging from 12 to 31 µg/L) were comparable to those found Dominguez Channel. Two of those measurements were qualified as BRL. Three of those copper measurements were qualified as BMDL.

Dissolved zinc concentrations also did not attain the water quality objective (69 to 297 µg/L) in all five of the five wet weather events sampled (Figure 4-3.17). Zinc concentrations were comparable to Dominguez Channel (median of 130 µg/L, ranging from 112 to 158 µg/L). Two of those measurements were qualified as BRL. Three of those zinc measurements were qualified as BMDL.

Total mercury measurements reported were above the human health water quality objective (0.051 µg/L) on one of the five events measured at during wet weather (Figure 4-3.12). As explained below (See Section 4.2.2 Correlation Analysis), the reported mercury measurements are believed to be biased high due to the laboratory method used.

PD 21-Hollypark Drain (TS22)

A summary of constituents not attaining Category 1 water quality objectives at the PD 21-Hollypark Drain Tributary Station during the 2008–2009 wet weather sampling is presented in Table 4-5.4.

Fecal coliform bacteria measurements were above the applicable water quality objective (400 mpn/100 ml) five out of five times sampled during wet weather in (Figure 4-3.7). However, the Dominguez Channel tributaries are subject to the high flow suspension of REC-1 and REC-2 beneficial uses and standards in accordance with the “tributary rule” of the Basin Plan, as applicable to the Dominguez Channel, for events 2008-09Event06, 2008-09Event09, and 2008-09Event21. Those events are not highlighted as non-attainment of water quality objectives in data tables.

Dissolved copper measurements were above the hardness-based water quality objective (10 to 61 µg/L) twice out of the five times measured (Figure 4-3.8). Dissolved copper concentrations (median 12 µg/L, ranging from 9 to 14 µg/L) were comparable to Dominguez Channel. One of those copper measurements above the water quality objective was qualified as BMDL.

Dissolved zinc measurements were above the hardness-based water quality objective (76 to 458 µg/L) once out of the five times measured (Figure 4-3.17). Dissolved zinc concentrations (median 64 µg/L, ranging from 42 to 74 µg/L) were somewhat lower compared to Dominguez Channel. The CTR allows an exceedance frequency of no more than once every three years for aquatic life criteria.

D.D.I. 8 (TS23)

A summary of constituents not attaining Category 1 water quality objectives at the D.D.I. 8 Tributary Station (D.D.I. 8) during the 2008–2009 wet weather sampling is presented in Table 4-5.5. The pH at D.D.I. 8 did not attain the upper limit of 8.5 established in the Basin Plan once out of the five times measured in wet weather events (Figure 4-3.14).

Fecal coliform bacteria measurements were above the applicable water quality objective (400 mpn/100 ml) five out of five times sampled during wet weather in (Figure 4-3.7). However, the Dominguez Channel tributaries are subject to the high flow suspension of REC-1 and REC-2 beneficial uses and standards in accordance with the “tributary rule” of the Basin Plan, as applicable to the Dominguez Channel, for events 2008-09Event06, 2008-09Event09, and 2008-09Event21. Those events are not highlighted as non-attainment of water quality objectives in data tables.

Dissolved copper measurements were above the hardness-based water quality objective (4 to 61 µg/L) four out of the five times measured (Figure 4-3.8). Dissolved copper concentrations (median 17 µg/L, ranging from 10 to 37 µg/L) were comparable to Dominguez Channel. Two of the measurements above the water quality objective were qualified as BRL, and two were qualified as BMDL.

Dissolved zinc measurements were above the hardness-based water quality objective (42 to 458 µg/L) twice out of the five times measured (Figure 4-3.17). Dissolved zinc concentrations (median 101 µg/L, ranging from 28 to 285 µg/L) were comparable to Dominguez Channel.

Dominguez Channel at 116th St. (TS24)

A summary of constituents not attaining Category 1 water quality objectives at the Dominguez Channel at 116th St Tributary Station (TS24) during the 2008–2009 wet weather sampling is presented in Table 4-5.6 and follows.

The pH at TS24 did not attain the upper limit of 8.5 established in the Basin Plan once out of the five times measured in wet weather events (Figure 4-3.14).

Fecal coliform bacteria measurements were above the applicable water quality objective (400 mpn/100 ml) five out of five times sampled during wet weather in (Figure 4-3.7). However, the Dominguez Channel tributaries are subject to the high flow suspension of REC-1 and REC-2 beneficial uses and standards in accordance with the “tributary rule” of the Basin Plan, as applicable to the Dominguez Channel, for events 2008-09Event06, 2008-09Event09, and 2008-09Event21. Those events are not highlighted as non-attainment of water quality objectives in data tables.

Dissolved copper did not attain the hardness-based water quality objective (4 to 61 µg/L) five out of the five times measured (Figure 4-3.8). Dissolved copper concentrations (median 36 µg/L, ranging from 29 to 71 µg/L) were higher compared to Dominguez Channel. One of the measurements above the water quality objective was qualified as BRL; the other four were qualified as BMDL.

Dissolved zinc did not attain the hardness-based water quality objective (42 to 458 µg/L) four out of the five times measured (Figure 4-3.17). Dissolved zinc concentrations (median 183 µg/L, ranging from 155 to 474 µg/L) were somewhat higher compared to Dominguez Channel.

Dry Weather

Project No. 1232 (TS19)

A summary of constituents not attaining Category 1 water quality objectives at the Project No. 1232 Tributary Station (TS19) during the 2008–2009 dry weather sampling is presented in Table 4-5.1. The pH at Project No. 1232 did not attain the upper limit of 8.5 established in the Basin Plan once out of the three times measured in dry weather events (Figure 4-3.14). Fecal coliform bacteria did not attain the applicable water quality objective (400 mpn/100 ml) in all three events sampled during dry weather in (Figure 4-3.7).

Total mercury measurements reported were above the human health water quality objective (0.051 µg/L) on one of the three events measured at Project No. 1232 during dry weather (Figure 4-3.12). As explained below (See Section 4.2.2, correlation analysis) the reported measurement of mercury above the water quality objective is believed to be due to bias added by the analytical method used.

PD 669 (TS20)

A summary of constituents not attaining Category 1 water quality objectives at the PD 669 Tributary Station (TS20) during the 2008–2009 dry weather sampling is presented in Table 4-5.2. The pH at TS20 did not attain the upper limit of 8.5 established in the

Basin Plan once out of the three times measured in dry weather events (Figure 4-3.14). Fecal coliform bacteria did not attain the applicable water quality objective (400 mpn/100 ml) in two of the three events sampled during dry weather in (Figure 4-3.7).

Total mercury measurements reported were above the human health water quality objective (0.051 µg/L) on two of the three events measured at PD 669 during dry weather (Figure 4-3.12). As explained below (See Section 4.2.2, correlation analysis) the reported measurement of mercury above the water quality objective is believed to be due to bias added by the analytical method used.

Project Nos. 5246 & 74 (TS21)

A summary of constituents not attaining Category 1 water quality objectives at the Project Nos. 5246 & 74 Tributary Station (TS21) during the 2008–2009 dry weather sampling is presented in Table 4-5.3. The pH at TS21 did not attain the upper limit of 8.5 established in the Basin Plan twice out of the three times measured in dry weather events (Figure 4-3.14).

PD 21-Hollypark Drain (TS22)

A summary of constituents not attaining Category 1 water quality objectives at the PD 21-Hollypark Drain Tributary Station (TS22) during the 2008–2009 dry weather sampling is presented in Table 4-5.4.

The pH at TS22 did not attain the upper limit of 8.5 established in the Basin Plan once out of the three times measured in dry weather events (Figure 4-3.14).

Fecal coliform bacteria did not attain the applicable water quality objective (400 mpn/ 100 ml) in one of the three events sampled during dry weather in (Figure 4-3.7).

D.D.I. 8 (TS23)

A summary of constituents not attaining Category 1 water quality objectives at the D.D.I. 8 Tributary Station (TS23) during the 2008–2009 dry weather sampling is presented in Table 4-5.5. The pH at TS23 did not attain the upper limit of 8.5 established in the Basin Plan twice out of the three times measured in dry weather events (Figure 4-3.14).

Dominguez Channel at 116th St. (TS24)

A summary of constituents not attaining Category 1 water quality objectives at the Dominguez Channel at 116th St Tributary Station (TS24) during the 2008–2009 dry weather sampling is presented in Table 4-5.6.

The pH at TS24 did not attain the upper limit of 8.5 established in the Basin Plan twice out of the three times measured in dry weather events (Figure 4-3.14).

Ammonia did not attain the Basin Plan limit for warm water aquatic life habitat (1.0 to 30 mg/L) once out of the three times measured at TS24 during dry weather.

Dissolved copper did not attain the hardness-based water quality objective (4.0 to 61 µg/L) twice out of the three times measured (Figure 4-3.8) in dry weather. Dry weather dissolved copper concentrations (median 27 µg/L, ranging from 18 to 68 µg/L) were higher compared to Dominguez Channel. All three measurements above the water quality objective are qualified as BMDL.

4.2.1.3 Summary of Measurements Not Attaining Water Quality Objectives

This subsection summarizes the measurements not attaining the water quality objective of water quality objectives described above. The discussion is divided between Mass Emission Stations and Tributary Monitoring Stations.

The table below sets forth all constituents for which one exceedance or more was measured at the mass emission stations during the 2008-2009 monitoring year. In urban watersheds (Ballona Creek, Los Angeles River, Dominguez Channel) an exceedance of copper and zinc was measured in at least one wet weather sampling event and an exceedance of fecal coliform was measured in at least one dry weather sampling event. Fecal coliform exceedances were found in almost all wet weather events in urban watersheds; some of these events (2008-09Event06, 2008-09Event09, and 2008-09Event21) were subject to the wet weather suspension of REC-1 beneficial uses. An exceedance of pH was measured in dry weather sampling events in the Los Angeles River and Dominguez Channel watersheds and cyanide was measured in at least one dry weather sampling event in the Los Angeles River watershed.

In the Malibu Creek and Santa Clara River watersheds, exceedances of fecal coliform were measured in wet weather sampling events and in the San Gabriel and Santa Clara River watersheds exceedances of fecal coliform were measured in at least one dry weather sampling event. In the Malibu Creek watershed, exceedances of sulfate and TDS were measured in at least one wet weather sampling event, and exceedances of sulfate were measured in dry weather sampling events. In the San Gabriel watershed, exceedances of pH and chloride were measured in at least one dry weather sampling event.

An exceedance of total mercury was reported in at least one wet or dry weather sampling event for some of these watersheds, but the reported measurement of mercury above the water quality objective is believed to be due to bias added by the analytical method used.

Summary of Constituents Not Attaining Water Quality Objectives at Least Once at Mass Emission Stations during 2008–2009.

More urbanized watersheds are indicated with italics in the table below.

Mass Emission/Watershed	Wet	Dry
Ballona Creek (S01)	Fecal coliform Dissolved copper Dissolved zinc Total mercury*	Fecal coliform Total mercury*
Malibu Creek (S02)	Fecal coliform Sulfate TDS Total mercury*	Sulfate Total mercury*
Los Angeles River (S10)	Fecal coliform Dissolved copper Dissolved zinc	pH Cyanide Fecal coliform
Coyote Creek (S13)	Fecal coliform None	pH Fecal coliform
San Gabriel River (S14)	Fecal coliform Total mercury*	pH Fecal coliform Chloride TDS
Dominguez Channel (S28)	Fecal coliform Dissolved copper Dissolved zinc Total mercury*	pH Fecal coliform
Santa Clara River (S29)	Fecal coliform	Fecal coliform

*Believed to be due to bias added by the analytical method used.

The table below sets forth all constituents for which one exceedance or more was measured at the tributary monitoring stations during the 2008-2009 monitoring year. The exceedances were similar to those found at the Dominguez Channel mass emission station, except that pH exceedances were also measured in wet weather samples at each tributary monitoring station except PD 21-Hollypark Drain, dissolved copper was measured in dry weather sampling events at the Dominguez Channel at 116th monitoring station, and an ammonia exceedance was detected in at least one dry weather sampling event at the Dominguez Channel at 116th monitoring station. Fecal coliform exceedances were found in almost all wet weather events in the tributaries to Dominguez channel; some of these events (2008-09Event06, 2008-09Event09, and 2008-09Event21) were subject to the wet weather suspension of REC-1 beneficial uses.

An exceedance of total mercury was reported in at least one wet or dry weather sampling event for some of these tributary stations, but the mercury exceedances reported are believed to be due to bias added by the analytical method used.

Summary of Constituents Not Attaining Water Quality Objectives at Least Once at Tributary Stations During 2008–2009.

Tributary/Subwatershed	Wet	Dry
Project No. 1232 (TS19)	Fecal coliform pH Dissolved copper Dissolved zinc Total mercury*	pH Fecal coliform Total mercury*
PD 669 (TS20)	Fecal coliform pH Dissolved copper	pH Fecal coliform Total mercury*
Project Nos. 5246 & 74 (TS21)	Fecal coliform pH Dissolved copper Dissolved zinc Total mercury*	pH
PD 21-Hollypark Drain (TS22)	Fecal coliform Dissolved copper Dissolved zinc	pH Fecal coliform
D.D.I. 8 (TS23)	Fecal coliform pH Dissolved copper Dissolved zinc	pH
Dominguez Channel at 116th St. (TS24)	Fecal coliform pH Dissolved copper Dissolved zinc	pH Ammonia Dissolved copper

*Believed to be due to bias added by the analytical method used.

4.2.1.4 Detection Limit Analysis

The monitoring and reporting requirements of the permit state that constituents monitored at mass emissions stations which are below the detection limit for 75 percent of the first 48 events monitored need not be further analyzed, except for annual confirmation sampling during the first storm of the wet season. A review of the data from 2006 to 2009 showed a significant number of organic constituents, listed in the table below, that were measured at least 17 times and as many as 22 times, and not detected at the method detection limit.

Most of the constituents in the table below have been monitored since 2003. Therefore, a careful review of the historic data going back to 2003 may reveal that the number of measurements is close to, if not already over, the threshold needed to justify reduced monitoring frequency.

Summary of Organic Constituents with 17 to 22 Events Measured and Not Detected at the Method Detection Limit between 2006 and 2009

1-2-4-Trichlorobenzene	4-Chlorophenyl phenyl ether	Diazinon	Isophorone
1-2-Benzanthracene	4-nitrophenol	Dibenzo(a-h)anthracene	Malathion
1-2-Dichlorobenzene	Acenaphthene	Dieldrin	Methoxychlor
1-2-Diphenylhydrazine	Acenaphthylene	Diethyl phthalate	Naphthalene
1-3-Dichlorobenzene	Aldrin	Dimethyl phthalate	Nitrobenzene
1-4-Dichlorobenzene	alpha-BHC	di-n-Butyl phthalate	N-Nitroso-dimethyl amine
2-4-5-TP-SILVEX	alpha-chlordane	di-n-Octyl phthalate	N-Nitroso-di-n-propyl amine
2-4-6-trichlophenol	Anthracene	Endosulfan I (alpha)	N-Nitroso-diphenyl amine
2-4-D	Atrazine	Endosulfan II (beta)	PCB-1016 (Aroclor 1016)
2-4'-DDD	Benzidine	Endosulfan sulfate	PCB-1221 (Aroclor 1221)
2-4'-DDE	Benzo(a)pyrene	Endrin	PCB-1232 (Aroclor 1232)
2-4'-DDT	Benzo(k)flouranthene	Endrin aldehyde	PCB-1242 (Aroclor 1242)
2-4-dichlorophenol	Benzo[b]fluoranthene	Endrin ketone	PCB-1248 (Aroclor 1248)
2-4-dimethylphenol	Benzo[g-h-i]perylene	Fluoranthene	PCB-1254 (Aroclor 1254)
2-4-dinitrophenol	beta-BHC	Fluorene	PCB-1260 (Aroclor 1260)
2-4-Dinitrotoluene	Bis(2-Chloroethoxy) methane	gamma-BHC (lindane)	Pentachlorophenol
2-6-Dinitrotoluene	Bis(2-Chloroethyl) ether	gamma-chlordane	Phenanthrene
2-Chloroethyl vinyl ether	Bis(2-Chloroisopropyl) ether	Glyphosate	Phenol

2-Chloronaphthalene	Bis(2-Ethylhexl) phthalate	Heptachlor	Promethryn
2-Chlorophenol	Butyl benzyl phthalate	Heptachlor Epoxide	Pyrene
2-nitrophenol	Chlordane	Hexachlorobenzene	Simazine
3-3-Dichlorobenzidine	Chlorpyrifos	Hexachlorobutadiene	Toxaphene
4-6-Dinitro-2-methylphenol	Chrysene	Hexachloro-cyclopentadiene	Methyl Tertiary Butyl Ether (MTBE)
4-Bromophenyl phenyl ether	Cyanazine	Hexachloroethane	Total recoverable phenolics
4-chloro-3-methylphenol	delta-BHC	Indeno(1-2-3-c-d)pyrene	

4.2.2 Correlation Analysis

The monitoring and reporting requirements of the permit require an annual analysis of the correlation between pollutants of concern and Total Suspended Solids (TSS). That direction addresses the following management question:

How much of the variability in constituent concentration is accounted for by variability in TSS?

Table 4-10 shows the results of a correlation analysis of all measured constituents, 2006 – 2009, vs. TSS. The analysis is grouped by watershed, with wet weather and dry weather samples analyzed separately. Shaded cells in Table 4-10 indicate constituents that have at least half of their variability predicted by variability in TSS (i.e., the coefficient of determination, or r-squared value is greater than 0.5).

This approach is an efficient way to screen all detected constituents for correlation with TSS, without generating scatter plots for all constituents. Some initial observations from this screening analysis include:

- Volatile suspended solids (VSS) are significantly correlated with TSS in all watersheds and during both wet and dry weather sampling events. TSS is a useful proxy for VSS.
- In many cases nutrients (organic carbon, nitrogen species, and total phosphorous) correlated with TSS.
- Among the constituents not attaining water quality objectives (discussed in Section 4.2.1 above), some correlated with TSS better than others:
  - Fecal coliform correlated with TSS during dry weather in the San Gabriel River and the Los Angeles River, and during wet weather in Malibu Creek.
  - pH did not correlate with TSS at any of the mass emissions stations.

— Dissolved copper and dissolved zinc did not correlate with TSS; however, total copper and total zinc did correlate with TSS at most mass emission stations during wet weather.

— Total mercury did not correlate with TSS at any of the mass emissions stations.

The fact that total copper and total zinc correlated well with TSS led to further investigation of the following management questions related to sources:

Do some watersheds have higher particulate metal concentrations than others?

This question is answered by comparing the slopes of best fit regression lines for different watersheds. In a plot of metal concentration (µg metal per L water) vs. TSS (mg sediment per L water), the slope of the best fit line (µg metal per mg sediment) provides an estimate of the metal concentration in suspended sediments transported by the watershed.

Some metals that are dominated by naturally occurring mineralogy rather than human-caused pollutants would be expected to have similar slopes among different watersheds. For example, Figure 4-5.1 shows that the slopes of the aluminum vs. TSS plots are very similar among the seven different mass emission stations. The same is true for plots of chromium vs. TSS (Figure 4-5.2) and iron vs. TSS (Figure 4-5.3). All three of those trace elements – aluminum, chromium, and iron – appear to have similar background concentrations in the watershed sediments.

In contrast, a plot of nickel vs. TSS from the Malibu mass emission station has a slightly higher slope and intercept compared to nickel vs. TSS plots from other watersheds. This may reflect the influence of dark-green minerals, such as serpentines, that are common in coast-range sediments.

Other metals that have substantial human contributions (e.g., copper, zinc, and lead) would be expected to have higher slopes in more urbanized watersheds. For example, the slope of the best fit line for copper vs. TSS at the Dominguez Channel mass emission station is significantly higher compared to other watersheds (Figure 4-5.5). The Los Angeles River and Ballona Creek mass emission stations are intermediate to Dominguez Channel and less urbanized watersheds such as Malibu Creek, Santa Clara River, and San Gabriel River. This likely reflects the transport of copper-enriched particles from roadways, which are impacted by residue from copper-containing brake pads that are pervasive in the U.S. auto fleet.

Zinc and lead show a similar pattern to copper (Figures 4-5.6 and 4-5.7). Dominguez Channel has the highest slope on the metal vs. TSS plots (i.e., greatest metal concentrations in particles); Los Angeles River and Ballona Creek are intermediate to Dominguez Channel and the less urbanized watersheds.

As with copper, higher concentrations of zinc and lead in sediments from urbanized watersheds are expected. Zinc is another “road wear” element, common in rubber found in car tires, and also as a sacrificial oxidant in galvanized steel that is common in the urban environment. Lead is often found enriched in road grit as a result of the decomposition of lost wheel weights. Lead paint in older buildings can be another source of lead in some urban environments.

Is a lack of correlation with TSS sometimes an important clue?

The fact that total mercury did not correlate with TSS was unexpected. Mercury is strongly absorbed to particles, like lead, and so would be expected to correlate well with TSS. Comparison of the total mercury to TSS plots from the mass emissions and tributary stations to mercury vs. suspended sediment concentrations (SSC) plots from the Guadalupe River, in Santa Clara County, revealed another observation that called into question the accuracy of the mercury analytical methods used to date (See Figure 4-6).

The Guadalupe River is downstream of New Almaden, which was at one time the largest mercury mine in North America. The Guadalupe River is a known source of mercury contaminated sediments to San Francisco Bay. Therefore, it is unexpected to see that some total mercury measurements at mass emission and tributary stations fall above the best fit Total Mercury vs. Total Suspended Sediment line for Guadalupe River. Either some watersheds and tributaries are carrying unexpectedly high concentrations of mercury in sediments, or the analytical results are in error.

Review of the analytical methods used in this annual monitoring program revealed that samples were analyzed for mercury by EPA method 245.1. That method relies on absorption of light by a vaporized sample. Method 245.1 is subject to false positives caused by interfering constituents, such as sulfide, chloride, and organic carbon, which also absorb light. Most of the reported mercury concentrations are qualified as estimates. More accurate methods, such as EPA Method 1631, that rely on fluorescence of light, rather than absorption, should be used in the future to present an accurate assessment of mercury concentrations in Los Angeles County watersheds.

Are there other important correlations besides TSS that indicate constituent sources or watershed processes?

A review of the previous (2007-2008) annual monitoring report and other data shows that selenium is consistently measured above the chronic (Category 2) water quality objective in Malibu Creek. There is no significant correlation between TSS and selenium at Malibu Creek, but other correlations can provide clues to selenium sources. Selenium correlates with both arsenic (Figure 4-7) and sulfate (Figure 4-8) at Malibu Creek. The association of higher selenium concentrations with higher arsenic and sulfate concentrations suggests a common source – possibly leaching into groundwater from minerals common to the California Coast Range, followed by groundwater seepage into tributaries to Malibu Creek.

Some nutrients (e.g., nitrogen, phosphorous) were correlated with TSS during wet weather in urbanized watersheds (See Table 4-10). This was observed at the Ballona

Creek, Los Angeles River, Coyote Creek, and Dominguez Channel Mass Emission Stations.

To summarize, correlation analysis has been used to evaluate key questions related to constituent sources. Correlations with TSS are useful for characterizing the difference between highly urbanized and less urbanized watersheds as metal sources (copper, lead, and zinc). The lack of an apparent correlation between mercury and TSS led to closer scrutiny of the mercury data, and the initial conclusion that mercury results may be biased high. Selenium correlations with sulfate and chloride suggest a common source, possibly mineral formation leaching by groundwater.

It was noted that in the tributary stations (TS19 – TS24), pH was significantly correlated with alkalinity. As discussed below, under sources, this is a natural and expected outcome based on the buffering capacity provided by calcium carbonate, magnesium carbonate, and other contributors to alkalinity. Low alkalinity caused by sudden storm flows can lead to low pH, while high alkalinity caused by seepage of heavily mineralized groundwater during dry periods when there is little dilution can lead to high pH.

4.2.3 Watershed Load Analysis

The LACFCD collected and analyzed TSS samples at all mass emission stations equipped with automated samplers for storm events of at least 0.25 inches of total rainfall. Several storms were also manually sampled for TSS at the Santa Clara Mass Emission station, although not required. The TSS concentration for each storm is shown in Table 4-7 and the total TSS loads for each mass emission station is shown in Table 4-8. An estimate of the total constituent loads for each mass emission station is shown in Table 4-9.

Constituent loads at each mass emission station were analyzed to determine if there was any correlation between storm events and the amount of constituent loads. Figure 4-4 shows the load trend analysis for mass emission stations. Some first-flush phenomena were observed, primarily with constituents associated with particulate matter. Also, storms with greater runoff volumes typically had larger constituent loads.

Long term temporal trends cannot be found by analyzing one year's worth of data. An analysis of historical long term temporal trends can be found in the 1994-2005 Integrated Receiving Water Impacts Report. Additional long term trend analysis will be conducted for the next Integrated Receiving Water Impacts Report.

The following conclusions were deduced from the 2008-09 loads analysis:

- First-flush phenomenon was observed for most constituents whose concentrations came either from their insoluble or suspended form (i.e., TSS, oil and grease, etc.) or from a combination of their insoluble or suspended form and their dissolved form (i.e., total metals). Generally, constituents accumulate during dry weather and wash off during the first storm event(s) of the year.

- In general, TSS concentrations were higher during wet weather than during dry weather sampling events.

- The total runoff volume and constituent loads at the Los Angeles River Monitoring Station were usually higher than at the other monitoring stations.

- With an area of approximately 825 square miles, the Los Angeles River has approximately two to twenty-five times the surface area of the other watersheds. This creates more potential for surface runoff pollution and likely explains, in part, the increased loads of constituents at the Los Angeles River Monitoring Station when compared to the other monitoring stations.

- The Los Angeles River had the largest TSS out of the seven mass emission stations monitored, although other watersheds sometimes had larger loads during particular storm events. San Gabriel River was the smallest contributor of TSS.

- Ballona Creek, Los Angeles River, San Gabriel River, and Coyote Creek exhibited first-flush phenomena for TSS. TSS concentrations tended to decrease with fluctuation over the season except at Malibu Creek, Dominguez Channel, and Santa Clara River.

- Los Angeles River, as the largest watershed in the monitoring area, had a calculated average percent rainfall discharge of 12.9 percent. The percent discharge is the total runoff volume from the event hydrograph (Appendix A) divided by the calculated event rainfall volume (rainfall multiplied by the watershed area).

- The watersheds with the most impervious land uses, Table 2-1, had the highest average percent rainfall discharges. Ballona Creek, Dominguez Channel, and Coyote Creek had the highest averages; 29.7 percent, 32.6 percent, and 25.1 percent, respectively.

- The watersheds with the most vacant land uses, Table 2-1, had the lowest average percent rainfall discharges. These were Malibu Creek, San Gabriel River, and Santa Clara River; 7.8 percent, 3.8 percent, and 0.2 percent, respectively.

- As shown in Table 2-1, the watersheds with the most impervious land uses had the highest average percent rainfall discharges. Ballona Creek, Dominguez Channel, and Coyote Creek had the highest averages; 29.7 percent, 32.6 percent, and 25.1 percent, respectively.

- Also as shown in Table 2-1, the watersheds with the highest percentage of vacant land uses had the lowest average percent rainfall discharges. These were Malibu Creek, San Gabriel River, and Santa Clara River; 7.8 percent, 3.8 percent, and 0.2 percent, respectively.

The following management questions were evaluated to begin to develop a more refined description of watershed processes:

How do loads vary over the course of the storm season?

This question is answered in Figures 4-4, 4-9, 4-10, 4-11, and 4-12. Figure 4-4 presents the major constituent loads for each mass emission station for all events sampled. Figure 4-9 presents the TSS concentrations for each mass emission station for all events sampled. Figure 4-10 portrays the TSS concentrations for each mass emission station. Figure 4-11 shows the mass emission loads of total suspended solids and Figure 4-12 depicts the mass emission loads of total dissolved solids.

Constituent Loads Example Calculation

At the request of the Los Angeles Regional Water Quality Control Board (LARWQCB), below is an example of the constituent loads calculation:

Site:	Ballona Creek Mass Emission Station
Storm event:	2008-09Event06
Constituent:	Alkalinity as $CaCO_3$
Concentration:	115.5 mg/L
Runoff Volume:	3395.1 acre-ft (3091.57 acre-ft Runoff + 303.49 acre-ft Base Flow)

1lb = 454 g
1g = 1,000 mg
1L = 0.03531467 ft^3
1 ft^3 = 2.2957 x 10^{-5} acre-ft

Constituent Load = (Constituent Concentration)(Runoff Volume)

Constituent Load = (115.5 mg/L)(2303.45 acre-ft)(1g/1,000 mg)(1 lb/454g)(1 ft^3/2.2957 x 10^{-5} acre-ft)(1L/0.03531467 ft^3)

Conversion factors

Constituent Load = 1,066,353.7 lbs.

How would the interpretation of constituent loads change when evaluated on a load per watershed area basis? Are the same loads trends discussed above true when normalized to watershed area?

These questions can be answered by calculating the load per unit area for each mass emission station. An example of this calculation was made using TSS data for

2008-09Event21. The rankings of watersheds based on TSS loads compared to rankings based on TSS loads per area are presented in the table below.

Ranking of Watersheds Based on TSS Loads

vs. Rankings Based on TSS Loads per Unit Area

	Rank (Loads)	Rank (Load / Area)	Watershed Area (miles^2)	TSS Loads (lbs)	TSS Loads / Area (lbs / mile^2)
Ballona Creek (S01)	2	1	89	4,353,162	49,022
Malibu Creek (S02)	4	4	105	1,624,195	15,469
Los Angeles River (S10)	1	2	823	25,863,691	31,445
Coyote Creek (S13)	3	3	149	2,776,890	18,687
San Gabriel River (S14)	5	6	451	1,113,543	2,471
Dominguez Channel (S28)	6	5	33	259,295	7,810
Santa Clara River (S29)	7	7	411	50,667	123

The ranking of watersheds based on total loads is somewhat different from the ranking based on loads per unit area. Some general observations based on this example from 2008-09Event21 include:

- Although the Los Angeles River had the highest overall TSS loads during 2008-09Event21, Ballona Creek had the highest loads per unit area.
- Ballona Creek produced much more sediment per square mile compared to Malibu Creek, even though the two watersheds have comparable areas.
- San Gabriel River produced much more sediment per square mile compared to Santa Clara River, even though the two watersheds have comparable areas.

Several factors affect sediment production per unit area, including degree of urbanization, stream morphology, activities within the watershed, topography, and event size. This example calculation does not address the many factors affecting sediment production rates per unit area. It simply serves to illustrate that loads trends, and the resulting interpretation of watershed function, can be different when loads are normalized to watershed area.

4.2.4 Water Column Toxicity Analysis

This subsection describes the water column toxicity results generated during the 2008-2009 storm season. Water column toxicity monitoring was performed at all mass emission sites in accordance with the Municipal Stormwater Permit. In total, four samples were analyzed for toxicity at each site. Dry weather samples were collected on January 13, 2009 (2008-09Event15), and March 24, 2009 (2008-09Event30). Wet-weather samples were collected during the first rain event of the season on November 4, 2008 (2008-09Event03) for all Mass Emission Stations, except Santa Clara River, and on November 25, 2008 (2008-09Event06) only for Santa Clara River, and during another rain event on February 5, 2009 (2008-09Event21), at all mass emission sites. The results obtained from these samples are found in Table 4-6a (dry weather) and Table 4-6b (wet weather).

A minimum of one freshwater and one marine species was used for toxicity testing, specifically *Ceriodaphnia dubia* (*C. Dubia*) (water flea) seven-day reproduction/survival and *Strongylocentrotus purpuratus* (*S. purpuratus*) (sea urchin) fertilization. Results calculated from the *C. Dubia* and *S. purpuratus* tests included the No Observed Effect Concentration (NOEC), 25 and 50 percent Effective Concentration (EC25 and EC50), 25 and 50 percent Lethal Concentration (LC25 and LC50), 25 and 50 percent Inhibition Concentration (IC25 and IC50), and toxicity unit (TU). NOEC is the highest concentration of toxicant that would cause no observable adverse effects on the test organisms, which means the values for the observed responses statistically are not significantly different from the controls. EC50 is the toxicant concentration that would cause an observable adverse effect on a quantal response (such as death, fertilization, germination, or development) in 50 percent of the test population under specified conditions.

A quantal response is an all-or-none response. For example, death is a quantal response because a test organism can only be either dead or alive after being exposed to the toxicant concentration in the test sample. When the observable effect is death, the term Lethal Concentration or LC is used in place of the term Effective Concentration or EC. Therefore, LC50 is the concentration that produces a 50 percent reduction in survival under specified conditions. When the observable effect is sublethal, such as mean young per female or growth, the term Inhibition Concentration or IC is used. For example, IC50 is the concentration that causes a 50% reduction in the selected sublethal biological response, such as fertilization.

TU is defined in the NPDES Municipal Permit as 100 divided by the calculated median test response, e.g. LC50 or IC50. A TU value greater than or equal to 1.00 is considered substantially toxic and requires a Phase I TIE. However, as discussed below, there is some disagreement between our biological testing laboratories as to how toxicity should be interpreted for the sea urchin, and which methodology for exposing that marine species to 100% sample concentration should be applied.

The following conclusions were deduced from the water column toxicity testing:

- *C. dubia* survival was affected by exposure to the first dry-weather sample collected from the Ballona Creek mass emission site on January 13, 2009 (2008-09Event15). Exposure to a concentration of 31.25% storm water caused a 25% reduction in a sublethal biological measurement of the test organisms, such as immobility. However, greater than 100% storm water would be needed to cause a 50% reduction. This suggests a nonlinear relationship between the potency of storm water and biological inhibition. Nevertheless, all mass emission sites had TU values less than 1.00 (Survival and Reproduction) for both dry weather events. Therefore, no Phase I TIE tests were required. Sea urchin fertilization was adversely affected by exposure to the dry-weather samples collected during both events. NOECs ranged from 6% during the first dry-weather event to 55.2% during the second dry-weather event, and TUs ranged from <1.00 to 2.41. Toxscan, Inc. (an affiliate of Kinnetic Laboratories, Inc.) analyzed the samples from the first dry-weather event. They reported by telephone to the LACFCD that the highest testable concentration due to the addition of hypersaline brine to the test organisms was about 50%. It was later learned by the LACFCD that addition of hypersaline brine is preferred over using sea salts on a 100% effluent concentration as the sea salts are toxic to embryos in the fertilization test. Given that, Kinnetic Laboratories, Inc. asserted that current science in this field indicates that a TU value greater than or equal to 2.00 would reasonably indicate substantial toxicity and warrant a Phase I TIE test. Therefore, no Phase I TIE tests were run for any samples from the first dry-weather event.

  The same principle was applied to the test results for the second dry-weather event. Those samples were analyzed by Nautilus Environmental Laboratories. Only one sample, Los Angeles River, was found to be substantially toxic, i.e. TU was equal to 2.41. Phase I TIE manipulations strongly suggested that trace metals were the primary constituent of toxicity. Ceriodaphnia dubia survival and reproduction were adversely affected by exposure to the wet-weather samples collected from several mass emission sites during the first wet-weather event, according to the IC25 and IC50 values. IC25 values ranged from 28.13 to 100%, and IC50 values ranged from 86.54 to 100%. A NOEC of 50% was observed for organisms exposed to samples collected from Malibu Creek. ABC Laboratories reported TU values of 1.16, and 1.06, respectively, for Survival and Reproduction for that site. Despite the small nature of the first wet-weather event at these sites (rainfall amounts ranged from 0.12" to 0.44"), a sufficient volume of representative flow-weighted samples was collected and transported to the Los Angeles County Environmental Toxicology Laboratory to conduct the initial toxicity and Phase I TIE tests. Unfortunately, the Environmental Toxicology Laboratory did not transfer enough sample volume to ABC Laboratories, so the Phase I TIE tests could not be conducted. The LACFCD will remind the

Environmental Toxicology Laboratory before each toxicity event to send enough sample water (typically 10 gallons) to the toxicity laboratories to conduct both tests. The TU values for Malibu Creek are highlighted in Table 4-6b.

- Sea urchin fertilization was adversely affected by exposure to the first wet-weather event samples collected at the Ballona Creek, Malibu Creek, Los Angeles River, Coyote Creek, and San Gabriel River sites on November 4, 2008 (2008-09Event03). NOECs of 50% or less were observed in organisms exposed to samples from those sites. These NOECS indicate that adverse effects were observed at half strength or less of storm water. The resulting TU values, which ranged from 2.20 to 3.29, are highlighted in Table 4-6b.

- ABC Laboratories analyzed samples from the above mentioned sites during several sampling events. Contrary to the practice of Kinnetic Laboratories and Nautilus Environmental, ABC Laboratories used sea salts to raise the salinity of the 100% sample solution to a level prescribed in the EPA test method. They were able to expose the test organisms to the 100% solution and the TU equation of 100/IC50 (or LC50) in the NPDES Municipal Permit was applied. Phase I TIE tests were warranted for the above mentioned samples. Despite the small nature of the first wet-weather event at these sites (rainfall amounts ranged from 0.12” to 0.44”), a sufficient volume of representative flow-weighted samples was collected and transported to the Los Angeles County Environmental Toxicology Laboratory to conduct the initial toxicity and Phase I TIE tests. Unfortunately, the Environmental Toxicology Laboratory did not transfer enough sample volume to ABC Laboratories, so the Phase I TIE test could not be conducted. The LACFCD will remind the Environmental Toxicology Laboratory before each toxicity event to send enough sample water (typically 10 gallons) to the toxicity laboratories to conduct both tests.

- Kinnetic Laboratories conducted the toxicity tests on all samples for the second wet-weather event on February 5, 2009 (2008-09Event21). They followed their testing practice mentioned above. In agreement with that practice, none of the samples were determined to be substantially toxic. All TU values were less than 2.00. Therefore, no Phase I TIE tests were warranted.

4.2.5 Trash Monitoring Analysis

The Municipal Storm Water Permit requires a minimum of one photograph at each mass emission station after the first storm event and three additional storm events per year. Pictures can be found in Appendix C.

Ballona Creek Watershed and Los Angeles River Watershed Trash Compliance Monitoring Reports can be found in Appendices I and J respectively.

4.2.6 Identification of Possible Constituent Sources

This section summarizes some of the key points about known or suspected sources of constituents that did not attain Category 1 water quality objectives.

4.2.6.1 Fecal coliform

The source of bacteria is hard to pinpoint. According to the Draft Total Maximum Daily Load to Reduce Bacterial Indicator Densities at Santa Monica Bay Beaches published on November 8, 2001, by the LARWQCB urban runoff from the storm drain system may have elevated levels of bacterial indicators due to sanitary sewer leaks and spills, illicit connections of sanitary lines to the storm drain system, runoff from homeless encampments, illegal discharges from recreational vehicle holding tanks, and malfunctioning septic tanks among other things. Fecal matter from animals, including pets, livestock and birds can also elevate bacteria levels. A July 2007 report by ENSR International for USEPA New England Region 1, Mitigation Measure to Address Pathogen Pollution in Surface Waters: A TMDL Implementation Guidance Manual for Massachusetts, reiterated the above-mentioned sources.

In addition to bacteria sources, certain factors can amplify bacteria concentrations by promoting bacteria growth. Organic carbon provides food for bacteria. Sunlight can kill off bacteria, and therefore cover water can promote bacterial growth. Slow moving, stagnant water can promote bacterial growth.

The Southern California Coastal Water Research Project (SCCWRP) has recently conducted bacteria source identification studies on Ballona Creek, published in 2005 in the journal Water Air and Soil Pollution. The City of Los Angeles has conducted a bacteria source identification study on the Los Angeles River, published November, 2008. Both of those studies confirm that there are dry weather urban runoff sources that discharge into the MS4; however, it is difficult to determine the exact sources of fecal coliform bacteria in the discharges to the MS4. The study by the City of Los Angeles also pointed out the role of bacteria re-growth and scouring of sediments with bacteria attached.

4.2.6.2 Copper and Zinc

According to the report *Regulating Copper in Urban Stormwater Runoff* by G. Fred Lee, Ph.D. and Anne Jones-Lee, Ph.D., Copper can come from brake pads or industrial (such as the textile industry) and mining sources. A metals source study is discussed in the article *Loadings of Lead, Copper, Cadmium, and Zinc in Urban Runoff from Specific Sources* by A.P. Davis, M. Shokouhian, and S. Ni. The study concludes that significant levels of metals were found from urban areas, especially in highway runoff. The abstract identifies important sources, such as building siding for Lead, Copper, Cadmium, and Zinc, vehicle brake emissions for Copper and tire wear for Zinc. Atmospheric deposition was also identified as an important source of Cadmium, Copper, and Lead. Details behind those findings can be found in the May 2005 Technical Report from SCCWRP entitled, *Contributions of Trace Metals From Atmospheric Deposition to Stormwater Runoff in a Small Impervious Urban Catchment*.

4.2.6.3 Cyanide

There are at least two possible sources of cyanide in surface waters. Cyanide can form at low levels as a byproduct of wastewater disinfection processes. A detailed study of cyanide formation in wastewater was published by Rula Deeb and other authors, in the

Proceedings of the Water Environment Federation, in 2004. This could account for the low levels of cyanide observed during dry weather in the Los Angeles River.

Prior to 2008–2009, larger, short-term measurements of cyanide above the water quality objective were observed in many other watersheds, including Malibu Creek and Ballona Creek. These measurements above the water quality objective may be the result of intense wildfires that occurred in the months prior to the sampling event. A publication in the January 2003 issue of *Chemosphere* by Timothy Barber and others shows that biomass burning during wildfires can cause cyanide to be present at concentrations above water quality objectives in stormwater.

4.2.6.4 Mercury

As noted above, mercury measurements above the water quality objective are believed to be the result of analytical error. However, in the event that some measurements above the water quality objective are still detected even after implementing improved analytical methods, a brief discussion of potential mercury sources is warranted.

The United States Environmental Protection Agency maintains a website on mercury issues, including sources, found at www.epa.gov/mercury. A potentially significant source of mercury in urban stormwater is deposition from the atmosphere. Mercury gets into the atmosphere after being released during coal combustion. The Western States Petroleum Association has also recently been investigating mercury in crude oil and mercury emissions from oil refineries at the direction of the San Francisco Bay Regional Water Quality Control Board; preliminary results from that study indicate that the majority of mercury in crude oil appears to be retained in solid waste or retained inside refinery equipment and not emitted to the atmosphere.

4.2.6.5 Sulfate and Selenium

Large quantities of greenish rock with amphiboles and sediment are found near the Mass Emission station in the Malibu Creek Watershed. The hillside is mainly composed of what appears to be very decomposed, somewhat grainy, greenish marine or lagoonal sediment/glauconite and less decomposed, greenish-brown shale with clear fossils and embedded detritus. These sediments are known to be sulfur bearing. Representative field samples gathered initially had a distinct moderate sulfur (musty, rotten eggs) odor. Sulfate concentrations can be largely attributable to the presence of eroded sulfur-rich sediment. Fungal and bacterial processes within the creek and surrounding areas may facilitate the release of sediment bound sulfur into the water column.

Weathering of sulfur-bearing minerals could also explain the elevated selenium concentrations in Malibu Creek. Selenium and sulfur often co-occur in natural mineral formations; both elements are in the same group (i.e., column) of the periodic table, meaning that they have similar chemical properties. The correlation of selenium with arsenic further supports mineral weathering as a potential source for these constituents.

Another potential sulfur source may be effluent from the nearby Tapia Water Reclamation Facility, found just upstream from the sampling site. Sulfur is used in wastewater processes such as flocculation. However, other sampling stations close to wastewater treatment plants did not show highly elevated sulfur concentrations. Tests and/or a review of effluent reports would be necessary to determine if the Plant's effluent was a significant contributor to the raised sulfur concentrations of these waters.

4.2.6.6 Chloride and TDS

An article titled Residential Sources of Contamination on EPA's website states that elevated levels of chloride may be a result of fertilizers, animal waste, industrial wastes, minerals, or seawater. Another common source of chloride is household water softening units, which use sodium chloride to regenerate ion exchange units used to remove magnesium from water. Chloride increases TDS concentrations.

4.2.6.7 pH

pH is a measure of the acid (or H+ ion) concentration in solutions. When the concentration of acid and base (or OH- ion) are exactly equal, the pH is equal to 7.0. Natural rainwater has a pH of approximately 5.5 – slightly acidic. As minerals dissolve into rainwater, the pH increases because of the "buffering" effect of minerals such as calcium and magnesium carbonate. Sources that can decrease pH below the water quality objective of 6.5 include illicit discharges (e.g., swimming pools, battery acid, other light and heavy industrial chemicals).

It is also possible that sudden rain events can bring the pH below 6.5, if the water sampled is not heavily mineralized. This would be expected in a watershed that is mostly hardscape, with little vegetation to provide detention or interaction with soils. Sudden influx of rainwater is the most likely explanation for the low pH observed during wet weather in some of the tributary stations (e.g., Project No. 1232, Project Nos. 5246 & 74, Dominguez Channel at 116th St.). The fact that more than half of the variability in pH is explained by alkalinity ($r = 0.74$, $r^2 = 0.54$) supports this explanation.

Conversely, pH above 8.5 could indicate highly mineralized waters, for example groundwater seepages that are not as diluted, especially during dry weather. A common human factor than can cause high pH in surface waters is the discharge of concrete wash water. Algal blooms can also cause elevated pH at night, due to increased production of carbon dioxide as algae respire at night.

4.2.6.8 Ammonia

Ammonia exists naturally in the environment and is also an important commercial and industrial chemical, according to the New York Department of Health (http://www.health.state.ny.us/environmental/emergency/chemical_terrorism/ammonia_tech.htm). It is used in agriculture (fertilizers), as a refrigerant, in water treatment processes, in cleaning products and in the manufacture of many products including other chemicals, plastics, textiles, explosives and pesticides. Ammonia is produced by the decomposition of organic matter. One particular ammonia source of interest is wastewater treatment plants. According to Water Supply and Pollution Control, by Warren Viessman, Jr. and Mark J. Hammer, there is an average of 24 mg/L of Ammonia-Nitrogen (NH_3-N) in biologically treated domestic wastewater that has not undergone denitrification.

4.3 RECOMMENDATIONS

This section summarizes some of the key findings and recommendations from the analyses presented in this report. The recommendations are organized around specific types of actions (e.g., monitoring improvements, source assessments).

4.3.1 Monitoring Methods

Several key recommendations for improving monitoring techniques result from this analysis. As they are recommended monitoring changes, they could be initiated by LACFCD, after appropriate consultation with the LARWQCB and Copermittees:

- Consideration could be given to whether a mercury analytical method with an appropriately low detection limit, such as USEPA method 1631 should be used to ensure accurate results.

- Although selenium does not have a Category 1 objective for comparison, the chronic (Category 2) objective in Malibu Creek may require a change in analytical methods. Consideration could be given to whether future analyses of selenium by USEPA method 200.8 (inductively coupled mass spectrometry) should specify use of interference-reduction technologies (USEPA, 2007). These new technologies, referred to by manufacturers as “collision cells” or “dynamic reaction cells” have been proven to eliminate high bias in the measurement of selenium.

4.3.2 Source Investigations

Several recommendations for source investigations can be made based on the results and discussion presented above. However, the responsibility for carrying out the source investigations needs to be determined. Therefore, the appropriate next step on these items is for the LARWQCB to contact the appropriate stakeholder to carry out the source investigations.

- A review of existing monitoring programs within the Malibu Creek Watershed should be conducted to determine potential sources of sulfate and selenium.

- To address trace metals, such as copper and zinc, in the Dominguez Channel, the next logical step is to conduct another year of tributary sampling in the Dominguez Channel watershed.

- In the Ballona Creek and the Los Angeles River, existing monitoring programs should address sources that increase trace metal (copper, zinc) concentrations in sediments transported by stormwater.

4.3.3 Information Development and Clarification

Information development activities can be carried out by LACFCD through completion of future reports and discussions with the LARWQCB and stakeholders.

- Consideration could be given to how MUN water quality objectives are to be implemented where MUN is a conditional use.

- The LARWQCB should review the EPA test method for estimating chronic toxicity of effluents and receiving waters to west coast marine and estuarine organisms, and current science in that field, and issue guidance on whether or not to use sea salts in the high effluent percentage test solution. Two of the three laboratories who conducted toxicity tests asserted that sea salts are themselves toxic to embryos in the sea urchin fertilization toxicity test.

- If use of hypersaline brine is the preferred methodology to sea salts for toxicity testing, then the LACFCD recommends that the LARWQCB issue new guidance on the applicable value of the Toxic Unit to use to indicate that a sample is substantially toxic. All three laboratories who conducted toxicity tests asserted that a value greater than or equal to 2.00 is most appropriate and will reasonably lead to conclusive Phase I TIE test results.